SPECIFICATION

BE IT KNOWN THAT WE, JAMES HUANG, WILLIAM CHOU and DAVID CHOU, all residing at c/o Yeu Ming Tai Chemical Industrial Co., Ltd., No. 11, 34th Road, Taichung Industrial Park, Taichung, Taiwan; and JUIN-YIH LAI, KUEIR-RARN LEE, DA-MING WANG, RUOH-CHYU RUAAN and TIAN-TSAIR WU, all residing at No. 22, Pu-Jen Road, Chung-Li City, Taoyuan, Taiwan, subjects of Taiwan, have invented certain new and useful improvements in

ASYMMETRIC POROUS POLYTETRAFLUOROETHYLENE MEMBRANE FOR A FILTER

of which the following is a specification:-

ASYMMETRIC POROUS POLYTETRAFLUOROETHYLENE MEMBRANE FOR A FILTER

BACKGROUND OF THE INVENTION

The present invention relates to an asymmetric porous polytetrafluoroethylene membrane for a filter. Also, the present invention relates to material for a filter comprising the asymmetric porous polytetrafluoroethylene membrane for a filter and a reinforcing material.

Porous polytetrafluoroethylene membrane (hereinafter referred to as porous PTFE membrane) has excellent chemical resistance and high tensile strength and therefore is suitably used for a variety of purposes such as a filter for filtering gas and liquid, an agent for an air permeable and water impermeable membrane for clothing and a sheet for medical use, in addition to a sealing or gasket for piping and production facilities in the fields of chemicals, foods and semiconductors.

A process for preparing a porous PTFE membrane is disclosed (for example see USP 3,953,566, USP 3,962,153, USP 4,096,227 and USP 4,187,390), in which PTFE paste, which is a mixture of PTFE fine powder and an extrusion aid such as naphtha, is extruded and then rolled. Then, after removing the extrusion aid from the rolled article, the article is drawn in a uniaxial or biaxial direction. Subsequently, to maintain the shape of the drawn porous PTFE membrane, heat-setting is conducted at a temperature between 35°C and the melting point of PTFE.

Also, many documents disclose using the obtained porous

PTFE membrane as a filter but the porous PTFE membrane disclosed in these documents have the problem that air permeability and collection efficiency is insufficient (for example see USP 5,234,739, USP 5,395,429 and USP 5,409,515).

SUMMARY OF THE INVENTION

The object of the present invention is to provide an asymmetric porous PTFE membrane for a filter having little change over time and conventionally known properties of a porous PTFE molded article such as water permeability resistance, air permeability, sealing properties and electric properties, in which collection efficiency, air permeability and pressure loss are improved.

The conventionally known porous PTFE membrane is continuously foamed and with respect to the formed pores, the pore diameter distribution is homogenous on the surface and inside the membrane and the pores are formed homogeneously over the entire membrane (porosity is almost constant in the membrane). That is, the conventionally known porous PTFE membrane is symmetrically porous.

As a result of intensive studies, water resistance, air permeability and water vapor permeability of a porous PTFE membrane were found to improve by forming an asymmetric porous PTFE membrane, in which one face of the membrane comprises a dense PTFE skin layer and the other face comprises a low density continuously foamed porous layer.

That is, the present invention relates to an asymmetric porous PTFE membrane for a filter comprising a dense skin layer and a continuously foamed porous layer, wherein

(1) the contact angle of water to the surface of said skin layer is 120 to 140°; and

(2) the diffuse reflectance of light is 91 to 94 %.

The asymmetric porous polytetrafluoroethylene membrane is preferably obtained by drawing in a biaxial direction.

The asymmetric porous polytetrafluoroethylene membrane for a filter preferably has a membrane thickness of 5 to 100 μm.

A material for a filter comprising the asymmetric porous polytetrafluoroethylene membrane for a filter preferably contains a reinforcing material comprising a synthetic resin or inorganic fiber.

The reinforcing material is preferably polyethylene, polypropylene, polyester, polyamide or glass fiber.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view depicting an example of the apparatus for thermal treatment.

Fig. 2 is a SEM image (magnified 3000 times) of the cross section of an asymmetric porous PTFE membrane subjected to thermal treatment (340°C, 10 seconds) on one side. The upper white area is the dense layer (heated layer).

DETAILED DESCRIPTION

The drawn porous PTFE membrane used in the present invention can basically be prepared from the six known steps described below.

(1) Step of extruding paste of PTFE fine powder

A paste mixture of PTFE fine powder obtained by emulsion

polymerization and an extrusion aid such as naphtha is extruded by an extruder to obtain an extruded article in the form of a cylinder, a rectangular column or a sheet.

The PTFE fine powder is powder obtained by coagulating an aqueous dispersion of a polymer obtained by emulsion polymerization to separate the polymer and then drying the polymer. The polymer is a tetrafluoroethylene (TFE) homopolymer or a copolymer of TFE and a small amount (usually at most 0.5 % by weight) of perfluoroalkyl vinylether or hexafluoropropylene (modified PTFE).

In this step, orientation of the PTFE is preferably kept as low as possible, in order to smoothly carry out the next drawing step. Orientation can be kept low by suitably selecting the reduction ratio (preferably at most 300:1, usually 20:1 to 150:1), PTFE/extrusion aid ratio (usually 77/23 to 80/20) and die angle of the extruder (usually approximately 60°) when extruding the paste.

As the extrusion aid, usually mineral oil having high lubricating properties such as naphtha is used.

(2) Step of rolling paste extruded article

The paste extruded article obtained in step (1) is rolled in the extrusion direction or a direction orthogonal to the extrusion direction using a calender roll to prepare a sheet.

(3) Step of removing extrusion aid

The extrusion aid is removed from the rolled sheet obtained in step (2) by heating or extracting with a solvent such as trichloroethane or trichloroethylene.

The heating temperature is selected depending on the kind of extrusion aid and is preferably 200° to 300°C, more preferably about

250°C. When the heating temperature is higher than 300°C, particularly higher than 327°C which is the melting point of PTFE, the rolled sheet tends to be baked.

(4) Drawing step

The rolled sheet from which the extrusion aid is removed obtained in step (3) is drawn. Drawing can be conducted in a uniaxial direction or a biaxial direction but drawing in a biaxial direction is preferable from the viewpoint of narrowing the distribution of pore diameter and obtaining porosity preferable for air permeability. Drawing in a biaxial direction can be conducted sequentially or simultaneously. Also, the rolled sheet may be pre-heated to approximately 300°C before drawing.

The drawing ratio influences the tensile strength of the membrane and therefore should be carefully selected. The drawing ratio is preferably 300 % to 2000 %, more preferably 400 % to 1500 %. When the drawing ratio is out of this range, the desired pore diameter and porosity may not be obtained.

(5) Heat-setting step

The drawn sheet obtained in step (4) is heat-set by thermal treatment at a temperature range of 340° to 380°C, which is slightly higher than the melting point of PTFE (about 327°C) but lower than the decomposition temperature of PTFE, for a relatively short period of time (5 to 15 seconds). When the temperature is lower than 340°C, heat-setting tends to be insufficient. When the temperature is higher than 380°C, the setting time becomes short and controlling the time tends to become difficult.

(6) Preparation of asymmetric porous PTFE membrane

In the present invention, an asymmetric porous PTFE membrane is prepared by cooling one face of the drawn symmetric porous PTFE membrane obtained in the above manner while heating the other face and then cooling the heated face. An example of the equipment and process for preparing the porous PTFE membrane are depicted in Fig. 1 but the equipment and process are not limited thereto.

Below, the preparation process in the present invention is explained in detail with reference to Fig. 1.

The symmetric porous PTFE membrane heat-set and cooled in step (5) is delivered from delivery roll 4 and passed between heater 2 and cooling brine bath 1. The surface temperature of the PTFE membrane is measured by temperature sensor 6 and read by temperature reader 7. Then, the data regarding temperature is sent to heater controller 8 and based on the data, the temperature of hot air discharged from heater 2 via hot air discharge port 3 is controlled. Liquid for cooling is circulated in cooling brine bath 1 to maintain a constant temperature. The PTFE membrane passed through these units is wound onto wind roll 5 for the asymmetric porous PTFE membrane.

The thermal treatment temperature provided by heater 2 is preferably 260° to 380°C, more preferably 340° to 360°C. When the thermal treatment temperature is lower than 260°C, formation of the dense layer tends to be insufficient. When the thermal treatment temperature is higher than 380°C, controlling preparation of the asymmetric PTFE membrane becomes difficult and the entire membrane tends to become dense.

On the other hand, the cooling treatment temperature

provided by cooling brine bath 1 is preferably at most 0°C, more preferably at most −10°C. When the cooling treatment temperature is more than 0°C, controlling preparation of the asymmetric PTFE membrane becomes difficult and the entire membrane tends to become dense, thereby decreasing air permeability.

The time for thermal treatment and cooling treatment is preferably 5 to 15 seconds, more preferably 6 to 10 seconds.

By cooling one face of the symmetric porous PTFE membrane heat-set by the above conditions, a continuously foamed porous layer is formed and by thermally treating the other face again at the same time, the membrane surface is modified to obtain an asymmetric porous PTFE membrane having a dense skin layer.

The dense layer refers to a layer, in which only one face of the membrane is modified to densify the porous structure further and which has properties different from the original symmetric membrane such as contact angle of water and diffuse reflectance of light. The continuously foamed layer refers to a layer having substantially the same porous structure as the membrane before thermal treatment.

Also, when 0.1 to 0.2 mL of an aqueous solution containing 60 % of n-propylalcohol is dropped on the surface of the porous layer which is not thermally treated, the aqueous solution immediately permeates into the membrane and the white surface of the porous layer appears to be transparent. On the other hand, when the aqueous solution is dropped on the surface of the thermally treated and densified skin layer, the aqueous solution does not easily permeate and the dropped surface maintains the original whiteness.

The contact angle of water to the skin layer of the asymmetric

porous PTFE membrane of the present invention is 120° to 140°, preferably 125° to 135°. When the contact angle is less than 120°, densification of the thermally treated face is insufficient and collection efficiency tends to decrease. When the contact angle is more than 140°, the skin layer is excessively densified and air permeability tends to decrease.

The contact angle of water to the asymmetric porous PTFE membrane is extremely high in comparison to the contact angle of water to a symmetric porous PTFE membrane (110° to 118°). This indicates that the skin layer of the asymmetric porous PTFE membrane of the present invention is superior in waterproof properties compared to a symmetric porous PTFE membrane.

Herein, the contact angle of water is found from the following equation.

$$\text{Contact angle} = 2\tan^{-1}(h/r)$$

In the equation, h represents the height of a spherical water drop and r represents the radius of a spherical water drop.

The diffuse reflectance of light of the skin layer of the asymmetric porous PTFE membrane for a filter of the present invention is 91 to 94 %. The diffuse reflectance is an index indicating the modified layer. Diffuse reflectance of less than 91 % indicates that densification is insufficient and diffuse reflectance of more than 94 % indicates that densification is excessive. The reflectance is high in comparison to the diffuse reflectance of light of a symmetric porous PTFE membrane (90 to 91 %).

According to observation of SEM images, the asymmetric porous PTFE membrane of the present invention has a dense skin layer and a porous layer having a porous structure similar to that of a conventional symmetric porous PTFE membrane, while the conventional symmetric porous PTFE membrane has the same porous structure over the entire membrane. The porosity of the entire membrane is preferably 30 to 95 %, more preferably 50 to 90 %. When the porosity is less than 30 %, pressure loss tends to increase and when the porosity is more than 95 %, collection efficiency tends to decrease.

Herein, the porosity is found from the following equation by measurement of density.

$$\text{Porosity (\%)} = [1-(\text{PTFE apparent density}/\text{PTFE true density})] \times 100$$

In the equation, PTFE apparent density (g/cc) = weight (W)/volume (V) of the porous PTFE membrane and PTFE true density (g/cc) = 2.15 (from literature).

The maximum pore diameter of the porous layer of the asymmetric porous PTFE membrane of the present invention is preferably 0.03 to 2 μm, more preferably 0.05 to 1 μm. When the maximum pore diameter is smaller than 0.03 μm, pressure loss tends to increase. When the maximum pore diameter is larger than 2 μm, collection efficiency tends to decrease.

Herein, the maximum pore diameter is calculated as follows.

First, the pore diameter and porous structure of the porous layer of the symmetric porous PTFE membrane and the asymmetric

PTFE membrane obtained by thermally treating a symmetric porous PTFE membrane are confirmed to be unchanged before and after thermal treatment from SEM photographs (magnified 20,000 times). One feature of the present invention is that after thermal treatment, the pore diameter and the porous structure of the porous layer remain unchanged and only the skin layer is modified.

Next, the maximum pore diameter of the symmetric porous PTFE membrane is measured by a Porosimeter and the obtained value is considered to be the maximum pore diameter of the asymmetric porous PTFE membrane.

A membrane sample is placed in the sample chamber of the porosity measuring machine (Porosimeter PMI-1500, made by Porous Materials Inc.) and measurement is started in the automatic mode. As soon as measurement begins, gas (nitrogen gas) is introduced to one face of the membrane in the sample chamber. The introduction rate of the gas is controlled automatically.

While the pressure of the introduced gas is low, the membrane sample functions as a barrier and the pressure inside the chamber gradually rises continuously. When the sample loses barrier properties due to high pressure, the gas begins to permeate through the sample. The pressure of the sample chamber then ceases to increase and the pressure is measured at this point.

The above measurement of pressure was conducted for a dried membrane and a membrane moistened with Porewick solution to find pressure P_1 and P_2 of each.

The Porewick solution is the product name of a standard solution having surface tension adjusted to 16 dyn/cm, available from

Porous Materials Inc.

The maximum pore diameter is found from the following equation.

$$d = C \cdot (\tau / \Delta P)$$

In the equation, d = the maximum pore diameter (μm), C = 0.415, τ = surface tension (dyn/cm) of the moistening solution and $\Delta P = P_2 - P_1$ (psi).

The thickness of the asymmetric porous PTFE membrane for a filter of the present invention is preferably 5 to 100 μm, more preferably 10 to 70 μm. When the membrane thickness is less than 5 μm, collection efficiency tends to decrease and when the thickness is more than 100 μm, air permeability tends to decrease. The thickness of the skin layer is preferably 0.04 to 40 %, more preferably 0.1 to 30 % of the total membrane thickness. When the thickness of the skin layer is less than 0.04 % of the total membrane thickness, collection efficiency tends to decrease and when the thickness of the skin layer is more than 40 %, pressure loss tends to increase.

A material for a filter using the asymmetric porous PTFE membrane for a filter of the present invention is described below.

The asymmetric porous PTFE membrane for a filter of the present invention is preferably used as a material for a filter by reinforcing one side or both sides of the PTFE membrane with mesh, woven fabric or non-woven fabric having high air permeability, from the viewpoint of maintaining function as a filter over a long period of time.

The reinforcing material can be combined with the PTFE

membrane by various methods such as partially adhering using an adhesive, needle punching and installing to the filter frame by merely placing thereon.

Examples of the reinforcing material are air permeable woven fabric, non-woven fabric or mesh of synthetic resin or inorganic fiber, as material which has high strength and is relatively chemically inert. Examples of the synthetic resin are polyethylene, polypropylene, polyester and polyamide and examples of the inorganic fiber are glass fiber and carbon fiber.

The asymmetric porous PTFE membrane for a filter of the present invention can significantly improve collection efficiency of fine particles in air without pressure loss. Also, in comparison to a symmetric porous PTFE membrane, the permeability rate of gas and liquid can be increased 2 to 4 times and the tensile strength can be increased 20 to 60 %, even though the porosity is almost the same.

Hereinafter, the present invention is explained in detail based on Examples, but the present invention is not limited thereto.

<Pore diameter>

The pore diameter was measured using SEM (MODEL S570, made by Hitachi, Ltd.).

<Porosity>

Weight (W) and volume (V) of the porous PTFE membrane were measured and porosity was found from the following equation.

$$\text{Porosity (\%)} = [1-(\text{PTFE apparent density} / \text{PTFE true density})] \times 100$$

In the equation, PTFE apparent density (g/cc) = W/V and PTFE true density (g/cc) = 2.15 (from literature).

<Maximum pore diameter>

The maximum pore diameter was measured using a porosity measuring machine (Porosimeter PMI-1500, made by Porous Materials, Inc.) in the automatic mode.

A dried membrane and a membrane moistened with Porewick solution (available from Porous Materials, Inc.) were measured to find pressure P_1 and P_2 of each and the maximum pore diameter was found from the following equation.

$$d = C \cdot (\tau / \Delta P)$$

In the equation, d = maximum pore diameter (μm), C = 0.415, τ = surface tension (dyn/cm) of the moistening solution and $\Delta P = P_2 - P_1$ (psi).

<Contact angle of water>

The contact angle of water was found from the following equation using a contact angle measuring machine CA-D made by Kyowa Interface Science Co., Ltd.

$$\text{Contact angle} = 2 \tan^{-1} (h/r)$$

In the equation, h = height of a spherical water drop and r = radius of a spherical water drop.

<Heat of crystal fusion>

Heat of crystal fusion was measured using a differential thermal analyzer DSC-7 made by Perkin-Elmer Inc. under a nitrogen

current of 60 cm^3/minute at a temperature increase rate of 20°C/minute. The higher the melting heat is the higher the crystallization degree of PTFE.

<Diffuse reflectance of light>

Diffuse reflectance was measured according to ASTM E308 (wavelength 400 to 700 nm) using Mini Scan XE Plus (made by The Color Management Company).

<Tensile strength of membrane>

Tensile strength was measured according to ASTM D-1456.

<Elongation at break of membrane>

Elongation at break was measured according to ASTM D-1456.

<Pressure loss>

Pressure loss was measured using MODEL 8130 made by TSI Co, Ltd. in an air flow rate of 35.9 L/minute at a differential pressure of 150 mmH_2O.

<IPA flow rate>

IPA flow rate was measured according to ASTM F-317.

<Frazier air flow>

Frazier air flow was measured according to ASTM D-726-58.

<Collection efficiency>

A porous PTFE membrane was set in filter holder MODEL 8130 (made by TSI Co., Ltd.). The air flow rate of the exit side was adjusted to 35.9 L/min by adjusting the pressure and air containing colloid particles having a particle size of 0.3 μm was filtered. After measuring the number of permeated particles with a particle counter, the collection efficiency was calculated from the following equation.

Collection efficiency (%) = [1-(concentration of permeated particles in downstream area)/(concentration of particles in air of upstream area)] × 100

<u>EXAMPLES 1 to 3</u>

A paste mixture containing 80 parts of PTFE fine powder prepared by emulsion polymerization and 20 parts of naphtha was extruded using an extruder at a reduction ratio of 80:1 to obtain a rod-shaped extruded article having a diameter of 18 mm. The rod-shaped extruded article was rolled in the extrusion direction using a calender roll having a diameter of 500 mm to obtain a rolled sheet having a width of 260 mm and thickness of 0.2 mm. The sheet was then heated to 260°C in an oven to remove naphtha. Thereafter, the sheet was pre-heated to 300°C and simultaneously drawn in a biaxial direction to a drawing ratio of 500 % in the rolling direction and a drawing ratio of 300 % in a direction orthogonal to the rolling direction. Maintaining this drawn state, the sheet was heat-set by heating at 340°C for 15 seconds. The sheet was then cooled to room temperature to obtain a symmetric porous PTFE membrane having a thickness of 20 to 25 μm, a maximum pore diameter of 0.5 μm and a porosity of 90 %.

Then, one face of the symmetric porous PTFE membrane was treated with the thermal treatment apparatus of Fig. 1, wherein the temperature of cooling brine bath 1 was maintained at -10°C, the temperature of hot air discharged from heater 2 via hot air discharge port 3 was respectively adjusted to 260°C, 300°C and 340°C, and the time for the membrane to pass through the hot air discharge port area was adjusted to 7 seconds, to obtain an asymmetric porous PTFE

membrane. The evaluation results are shown in Table 1.

COMPARATIVE EXAMPLE 1

The symmetric porous PTFE membrane obtained in Example 1 was used. The evaluation results are shown in Table 1.

TABLE 1

	Ex. 1	Ex. 2	Ex. 3	Com. Ex. 1
Thermal Treatment Temperature (°C)	260	300	340	-
Membrane Thickness (μm)	20	23	25	25
Porosity (%)	85.8	89.8	90.9	89.7
Pore Diameter (μm)	0.09 to 0.17	0.08 to 0.15	0.09 to 0.19	0.10 to 0.19
Contact Angle of Water (°)	128	129	131	117
Light Reflectance (%)	92.4	92.6	93.8	90.8
Tensile Strength of Membrane (MPa)	5.96	7.3	8.5	5.07
Elongation at Break of Membrane (%)	109	134	107	166
Frazier Air Flow ($\times 10^4 ft^3/min \cdot ft^2$)	14.7	30.1	33.6	8.7
IPA Flow Rate ($ml/min \cdot cm^2$)	5.1	11.8	10.8	2.6
Pressure Loss (mmH_2O)	150.7	150.7	150.8	150.7
Collection Efficiency (%)	99.8	99.9	99.8	71.6

The present invention relates to an asymmetric porous PTFE membrane for a filter. Also, the present invention relates to material for a filter comprising the asymmetric porous PTFE membrane for a filter and a reinforcing material.